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By THOMAS GAFFIELD.

[A communication to the Chemical Section of the AMERICAN ASSOCIATION for the ADVANCEMENT OF SCIENCE, at its meeting in Boston, August 27, 1880. Reprinted from the PROCEEDINGS of the Association, Vol. XXIX.]

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THE ACTION OF SUNLIGHT ON GLASS.

By THOMAS GAFFIELD, of Boston, Mass.

WHEN God made the light, He created one of the most ethereal and yet most powerful of the elements and forces of nature.

It will be my pleasure to show how the sun, its great fountain and source, while it paints so beautifully and wonderfully the birds, the insects and the flowers, can in some measure also delicately tint the wares upon our tables, the glass in our houses, and the windows of the storied cathedrals of the world.

My subject is the action of sunlight in changing the color of glass, and I shall give a brief account of my humble experiments, commenced in 1863, and continued to the present day.

There is no mention of the subject in ancient records, for there was little need or use of glass windows in the olden time, and probably little or no glass of composition or color liable to any very perceptible change of tint. Not until after the beginning of the present century was the phenomenon observed in Europe, in the change of some light colored plate glass to a purple and of

another kind to a yellowish hue. In 1823, and the following year, Faraday, Bontemps and Fresnel made a few brief experiments showing that exposure to sunlight effected this change of color.

Other experiments were made by Melloni and Hunt, showing the action of glasses of different colors as media in the transmission of light and heat, but none to my knowledge are recorded up to 1863, with the above exceptions, showing the effect produced on the glass itself. The observations upon the subject by Pelouze (who for many years was the chemist of the French Plate Glass works at St. Gobain) are published in the Comptes Rendus for January 14, 1867.

Without making any pretension to the learning of the schools, or accurate scientific knowledge, I believe that my experiments, suggested by my experience as a glass-dealer and manufacturer, are original in their method and extent, as they cover the whole field of glass-making, including both colored and colorless glass. Those in connection with colored glass are entirely new.

By colorless glass is intended glass like that which we see in our windows, which shows little or no color in looking through its surface; but, observed through the edges, exhibits a great variety of tints, running from the almost colorless white to those of yellow, blue and green. The really colored glasses — made so intentionally by the addition of some metallic oxide, or other coloring constituent — can only be observed through the surface, as their opacity, except in the lightest colored specimens, will not allow an observation through the edges for more than a fraction of an inch. My experiments have been carried on chiefly upon the roof and upper window-sills of my house in Boston, in a position exposed to the full force of the sun's rays during the greater portion of every day, being protected by covers only in the event of snowstorms. Of course, a perfect arrangement could only be made when a flat roof or platform in an open field could be provided, and the sunlight could act with full force during every hour and minute of the day.

But mine was sufficiently near this point to show very interesting results. The change in color in some specimens is developed slowly, while in others it commences after a few hours of exposure in a summer day. In some sensitive kinds, I have witnessed a perceptible change in a single hour of sunlight exposure upon the top of a post in a country garden, at noontime, on a clear and hot day of August.

The glass plates exposed vary from four by two inches (my usual size) to four by eighteen, and from one-sixteenth of an inch to an inch in thickness. I have in my cabinet more than a thousand specimens showing the effect of exposure from a single hour to thirteen years.

I have thus exposed and tested some eighty kinds of colorless glass of American, English, French, German, and Belgian manufacture; embracing rough and polished plate; crown and sheet window glass; flint and crown optical glass; glass ware and glass in the rough metal. I have also exposed ground and opal glass, and some seventy kinds of colored sheet and rolled cathedral glass, including not only the main spectral colors,—red, orange, yellow, green, blue and violet,—but a variety of intermediate tints, such as brown, olive, amethyst, flesh color, etc.

I cannot in these brief moments give you all the privately recorded details of the interesting results of these experiments; but referring you to Silliman's Journal for 1867, for an account of the same up to that date, I shall rather hasten to allow my illustrations to tell their own story, which they will do without any color of exaggeration.

Various are the tints of the original colorless specimens, and equally various are those which are produced by sunlight exposure.

The nomenclature of different observers might also vary. I cannot recapitulate the long list from my journal, but would name as a general classification of the results produced, the following changes of color:

1. From white to yellowish.
2. From greenish to yellowish-green.
3. From brownish-yellow and greenish tints to various tints of purple.
4. From greenish-white to bluish.
5. From bluish and other tints to darker tints of the same colors.

Every specimen of colorless glass exposed for ten years has changed in color or tint, except some white flint glass, such as is used for fine glass-ware and optical glass. The optical glasses exposed—with the exception of two specimens of crown glass, containing no oxide of lead, which became of a yellowish hue—changed only in a very slight degree in tint, even after more than ten years of exposure, and not enough to be witnessed by ordinary

observers, or seriously to interfere with their practical value and use.

In some instances, where lenses seem to be affected, the change may be traced to a discoloration of the Canada balsam, by which the crown and flint glasses of the lens are cemented together. Bontemps thinks that this almost unique character of fine flint glass shows that the presence of oxide of lead, which enters largely into its composition, exercises a protecting influence against the coloring action of the sun's rays. I have proved by actual experiment that un-annealed as well as annealed glass can be changed in color by sunlight exposure.

Diffused light will also color glass, but with a greatly diminished effect, corresponding to its diminished power, as compared with the direct rays of the sun. Different degrees of coloration are sometimes noticed in the panes of the same window, and sometimes in the same pane, corresponding to their different degrees of sensitiveness to sunlight coloration, or differences of exposure to the direct rays of the sun.

That there comes a time when this coloring action of sunlight ceases, I have demonstrated by finding no further change by a second long exposure of glass removed from a building in which it was exposed for thirty-four years. The period of its duration varies with different glasses, the yellow coloration being chiefly developed in a year, increasing slowly afterwards, and almost entirely ceasing in some instances in ten years, while the purple tinted specimens develop less rapidly, and go on increasing in depth of color beyond this period. The continuance of my experiments for another decade or score of years, if my life should be preserved, will enable me to speak more definitely upon this point.

It is a curious fact that while these various glasses, with a few exceptions among the colored specimens, can be submitted before sunlight exposure to great heat in a glass-stainer's kiln without suffering any change, they can, after sunlight exposure, be restored to their original color by being placed in the kiln during a single fire. A second exposure to sunlight will reproduce the same yellow, purple and other colors as before, and this process of coloration by light and decoloration by heat can be carried on indefinitely. I am indebted for this observation to Pelouze, who names it in his essay in 1867, and I have confirmed its accuracy by many experiments since that date. Professor Percy also made

the same observation to the editor of the London Photographic News at about the same date, having ascertained the interesting fact in the laboratory which he occupied at the Museum of Practical Geology in London.

The most tangible illustration of change in colorless glass, as observed in similar windows in London, by Faraday in 1823, can be witnessed in the purple-tinted panes of some of the houses in Beacon street, in Boston, which were built fifty or sixty years ago. Some of the present owners and occupants formerly supposed that they were imported of the same color which we now observe, as an intentional decoration of their pleasant homes, and they were quite skeptical when I first published the statement that they were painted by the magic pencil of the sun. They have generally been convinced by the testimony of experiments which speak for themselves.

In speaking of experiments with colored glass, I should say that some kinds—called pot-metal, because colored in the pot—are colored throughout the body of the glass, while in the flashed, stained and enamelled specimens, the colors are upon the surface only.

In experiments continued for ten years with the main spectral colors, no change was found in any pot-metal specimens, except a slight darkening of the violet.

A change was observed in the colorless body of some of the flashed and stained pieces, a yellowish or purplish color being produced when the colorless side was uppermost, and also when the colored surface first met the sun's rays, and transmitted them in differing degrees to the colorless body below. The sunlight coloration of these flashed specimens is not sufficient to be noticed in an observation through the surface only.

In 1870, I commenced experiments with pot-metals, not of the primary colors, but of the intermediate ones which most nearly approach those produced in colorless glass by sunlight exposure.

In many specimens of the brownish, amber, purple and flesh colors thus exposed, I was surprised to observe the change in color or tint in a short time, a few days in summer sometimes sufficing to show the commencement of the sun's action. I have continued these experiments with colored glasses to the present day, and find the general results as follows:

The main colors, except violet, which is rendered a little darker

by exposure, are not at all affected, but the following changes are notable:

1. From brownish tints to a flesh color.
2. From flesh color to tints of purple or violet.
3. From amber, olive, and purple to darker tints of the same colors.

The result of these experiments led me to believe that they might furnish a key to solve interesting questions concerning the alleged superiority of the old cathedral windows, and I made a trip to Europe in 1872, to visit these interesting edifices, and, if possible, obtain some of the old glass. By removing the protecting putty from the edges of purple-tinted panes in Beacon street, one can observe the original color of the glass. I hoped to do the same with fragments from the old cathedrals. But the protecting edges of the lead divisions were so narrow, being generally not over one-eighth or one-sixteenth of an inch, that they afforded no chance for a similar observation. Obtaining specimens from Strasburg and elsewhere, I applied also the interesting heat test by dividing some of them in two pieces, and exposing one to the heat of a glass-stainer's kiln. But while some ordinary and expected effects were produced, such as the deepening of some red and yellow tints by a second firing, no change was produced in the pot-metal colors by heat which indicated any previous change by sunlight, except in the few small purple and flesh colored specimens. The colorless body of the flashed and enamelled glasses, with one exception of a slight lightening of the tint, was unchanged, being generally of so dark a color originally, that it seems no change could be effected by light or heat. So far as these purple and flesh colors, and other easily changing tints of pot-metal colors, were used in the old windows, and as the same cause must always produce the same effect, we can certainly say that they must have been changed in color or tint by their centuries of exposure, and that we cannot see to-day the glass as it was when it came from the artists' studios and the glass factories of the mediæval ages. And so far we may transfer some of our praise from the old artists in glass to the silent but wonderful pencil of the sun. But we must not make too much of this point, as an examination of many cathedrals in England, and on the continent, convinced me that the proportion of these peculiarly sensitive tints of flesh and light purple colors in most of their windows was small, being confined

chiefly to the faces and limbs of the Madonnas and saints, and many of these being produced in enamelled or flashed glass rather than pot-metal.

We may, perhaps, properly digress for a moment to say that the true cause of the superiority of these old cathedral windows, speaking paradoxically and yet truly, is found in the inferiority of the glass, its richness in the poverty of its constituents, its very perfection in its uneven thickness and the imperfections of its surface and its body, all covered as they are by the accumulating dust of ages and honeycombed by the corroding tooth of time. Like the facets of a diamond or ruby, each little wave and thread and blister becomes, by interference, refraction and reflection of the light which plays upon it, a new source of the gemlike brilliance, harmony, and beauty which distinguish the painted glass of former centuries.

The glassmakers of Berkshire and England aim to reproduce in some measure the perfection of this old glass, by reproducing its imperfections in the antique and rolled cathedral glass which are so extensively used by the artists and architects of to-day.

And now, what the wonderful alchemy of the sunlight is, and what the methods of its operations, are questions on which various opinions have been given by glassmakers and scientific men, but which only a careful consideration and comparison of the observations and theories of many practical and scientific observers can accurately decide. Some have attributed one or another of these colorations to the presence of oxide of iron, some to arsenic, and some to carbon or sulphates in the constituent materials of the glass.

The greater number think oxide of manganese, singular as it may seem, used as a decolorizer, to be the great colorist in all of these changes. In many colored and colorless glasses, and especially in those which assume after exposure any tint of purple or flesh color, it undoubtedly plays a very important part. But in some experiments with glass said to contain no manganese, decided changes of color from greenish to yellow have been produced. Perhaps the question cannot be accurately solved, until some glass manufacturer or lover of science and scientific truth shall make, with great care and for this special purpose, a series of colored and colorless glasses, which shall be exposed for months and years to the influence of sunlight. Knowing the exact con-

stituents of each specimen, a good foundation would be laid for a thorough scientific investigation of the subject. This has never yet been done, and in the absence of such knowledge, we can only theorize upon the results which we witness.

While I may not theorize, I may help others to do so by stating the interesting part which some metallic oxides play in coloring, and the oxide of manganese in decolorizing glass. In almost all kinds of window glass and glass-ware, materials are necessarily used which are not perfectly and chemically pure.

The sand, the carbonate or sulphate of soda, the lime and other constituents, one or all, contain slight impurities, and almost always oxide of iron.

The protoxide of this metal gives glass a bluish or bluish-green tint, the peroxide a yellowish, and a mixture of the two, in which condition it is generally found in glass, produces the almost universal greenish tints which we witness in the glass of commerce. To correct in some measure the coloration by iron, a small proportion of oxide of manganese, called "glassmakers' soap" is put into the "batch," or glass mixture. The natural tint produced by manganese in a high state of oxidation is purple or violet, and we cannot produce these colors without its use. In proportion as it is deprived of oxygen, it loses its coloring power, and when it reaches the state of protoxide, it becomes nearly colorless.

Now in the reaction which takes place in the melting-pot, the manganese gives up a portion of its oxygen and its coloring power to the iron, which is converted into peroxide, which gives a yellowish color to the glass.

This yellow color is complementary to whatever of purple coloring power is left in the manganese, and is therefore neutralized, and the glass comes out of a light color. When the sunlight strikes this glass, the nice balance between the oxygen of the iron and the manganese is disturbed, and there ensues, even in so solid a body as glass, an interesting contest for the possession of the coveted oxygen, and the conquering element is known and announces its victory by a display of its special colors. Every change of color or tint involves the wonderful condition, invisible to human eyes, of a molecular or inter-molecular movement of the atoms of this solid body, and it is probably attended by two circumstances: an interchange or redistribution of the oxygen among the constituents of the glass, and the development, in consequence of this

redistribution, of the special coloring power of the metallic oxide which has the greatest affinity for oxygen, or stands in the greatest proportion to the other constituents.

And so in some specimens the yellow of the iron predominates, in some the purple of the manganese, and in others, the yellow at first appears, and afterwards a yellowish purple and purple fully developed.

While these suggestions may help to explain the sunlight coloration of the so-called colorless glasses, they may apply also to colored glass, inasmuch as all of the sensitive specimens contain a certain proportion of iron, or manganese, or both.

If this coloring power of the sunbeams has not been generally known, it is because it cannot readily be seen by ordinary observers, except in such as the purple-tinted windows of Beacon street, and even then it may sometimes require the background of a light colored curtain.

The discovery of the defect is an annoyance to both consumers and glassmakers. When our Beacon street friends could no longer obtain similar glass to replace broken panes, the insertion of colorless ones gave their windows the interesting checker-board appearance which we witness to-day. When the glassmakers found the defect a matter of scientific observation and experiment, and their results published at home and abroad, they remedied the difficulty in a measure by using purer materials, or reducing the proportion of manganese in their "batch," or giving up its use entirely, preferring to have the glass assume its natural and more permanent color, even if it be a little greenish or bluish, rather than by "doctoring" the mixture,— to adopt the glass-makers' term for the use of manganese,— to have it light colored to-day and easily affected by the sunlight of to-morrow.

This improvement is of especial importance to photographers, who, in all operations requiring short exposures and all the light possible to obtain, would avoid the use of any glass in their skylights which, after a few months or years of exposure, will be robbed of a great proportion of its power to transmit the chemical influence of sunlight by a change to a yellow or purple tint, which in time might cut off almost as much actinic effect as if it had been ground or enamelled on one of its surfaces.

I have made some photographic experiments to show this deteriorating effect, by exposing sensitive paper under glasses of the

original colors, and those of the same kind, changed by sunlight exposure, and witnessing the perceptibly different shades of darkening produced. This action of sunlight must not be confounded with that called "rust," or "stain," which is occasioned in some glasses having an excess of alkali in their composition, by exposure to the atmosphere, and manifests itself in two ways; first, by a disintegration and roughening of the surface, sometimes producing all the effects of ground glass; and secondly, by an efflorescence and apparent formation of an infinitesimal coating of oxide upon the surface, on which the play of the sun's rays produces all the colors of the rainbow, as with the action of light on the infinitesimal grooves of mother-of-pearl. This is simply surface action, whereas the action of sunlight permeates the whole body of the glass wherever the rays directly strike it.

I might refer to many other points in connection with my subject, but my time will not permit and I hasten to exhibit the results of my experiments, asking my hearers, who are so much better versed in scientific studies than myself, to give me their light in ascertaining the causes and exact operations of this interesting power of the sun's rays to paint the products of art, as they do so beautifully and wonderfully the works of nature on the mountain, in the forest and field.

The large number of specimens of colored and colorless glasses here exhibited show the coloring effect of exposure to sunlight.

A tangible illustration of this subject is found in the purple-tinted windows of some of the Beacon-street houses, of which the specimens exhibited show the original color and the changes produced by sunlight exposures varying from one day to fifty years. These examples also show how this action can be turned to interesting account in impressing upon colored and colorless glasses the forms of leaves and ferns, and in printing inscriptions and mottoes. It is a species of photographic work with sensitive glass, instead of sensitive paper, the sun showing itself a most excellent printer and developer, and, indeed, the only true photographer in colors.

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